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New aspects of relationship between the enthalpies of fusion of aromatic compounds at the melting temperatures and the enthalpies of solution in benzene at 298.15 K. Part I

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ABSTRACT

In the present work the relationship between the enthalpies of fusion at the melting temperatures and the enthalpies of solution in benzene at 298.15 K of aromatic compounds is discussed in details. The difference between the fusion enthalpy at the melting temperature and the solution enthalpy at 298.15 K is determined by the temperature dependence of the fusion enthalpy, the solution enthalpy of the compound in the hypothetical liquid state at 298.15 K and the enthalpies of solid–solid phase transitions occurring between 298.15 K and the melting temperature. The latter contribution into the difference can be measured directly. The first two contributions were analyzed in a series of 17 aromatic compounds which do not exhibit solid-solid phase transitions between 298.15 K and the melting temperature. We calculated the fusion enthalpies at 298.15 K of these compounds in two different ways. On the one hand, they were derived from the fusion enthalpies at the melting temperature according to Kirchhoff's law using experimental data on solid and liquid heat capacities. It was assumed that the linear temperature dependence of melt heat capacity can be extrapolated down to 298.15 K. On the other hand, the fusion enthalpies at 298.15 K were calculated from the solution enthalpies in benzene at 298.15 K of the compounds in solid and hypothetical liquid states. Good agreement between the fusion enthalpies at 298.15 K calculated in different ways was demonstrated.

The solution enthalpies of eight solid and six liquid aromatic compounds in benzene at 298.15 K and the fusion enthalpies of two aromatic compounds were measured.

1. Introduction

Thermodynamic properties of organic liquids below the melting point play significant role in estimation of phase equilibrium parameters. Particularly, the knowledge of temperature dependence of fusion enthalpy is necessary for the accurate calculation of the ideal solubility (activity in saturated solution) of solid compounds [1]. This dependence is determined from the isobaric heat capacities of liquid ($C_p^{A_i}$ (l, T)) and solid ($C_p^{A_i}$ (cr, T)) phases of the compound of interest. In most cases $C_p^{A_i}$ (l, T) below the melting temperature is unknown and can be hardly determined directly [2], especially for compounds which have high melting temperature (above 450 K) and decompose or evaporate during melting. Therefore, various methods of estimation of the difference $\Delta_{cr}^{l}C_p^{A_i}$ (T) = $C_p^{A_i}$ (l, T) – $C_p^{A_i}$ (cr, T) have been tested in the last decades. Often the difference between the isobaric heat capacities of the liquid and solid phases is neglected [3–6]. Sometimes this difference is assumed to be close to fusion entropy [7–9] or to one-half of fusion entropy [10,11]. Such approximations lead to significant errors in solubility estimation when the melting temperature of the studied compound is high [1,12]. In the work [13] the molar heat capacity changes of dissolution in water at 298.15 K were used instead of the $\Delta_{cr}^{l}C_p^{A_i}$ (T) values for sugars and polyols. Empirical models also exist for estimation of the $\Delta_{cr}^{l}C_p^{A_i}$ (T) value [10,14]. However, the ambiguity in accounting the temperature dependence of fusion enthalpy remains.

Fusion enthalpy at 298.15 K ($\Delta_{cr}^{l}H^{A_i}$ (298.15 K)) together with vaporization enthalpy at 298.15 K obtained from the vapor pressure temperature dependencies [15] or determined using correlation gas chromatography [16] are used for estimation of sublimation enthalpy at the standard conditions. On the other hand, the vapor pressures of liquids at the standard conditions are required by the models describing the distribution of chemicals

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